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ELECTRODES OF SOLID METALS REPLACING THE DROPPING-  
MERCURY/ELECTRODES.

[Collated Report]

Various solid electrodes have been successfully used in polarographic analysis. This includes stationary and rotating microelectrodes (E. M. Skobets and F. A. Kachanova, Zavodskaya Laboratoriya, Vol. XIII, No. 2, 1947) and the polarisable electrodes described by Miller (Trudy Vsesoyuznoy Konferentsii po Analiticheskoy Khimii - Transactions of the All-Union Conference on Analytical Chemistry - , Vol. II, p. 551, 1943). In Zavodskaya Laboratoriya (Plant Laboratory), Vol. XIV, pp. 131-137, 1948, E. M. Skobets, L. S. Berenblyum, and N. N. Atamanenko of the Institute of General and Inorganic Chemistry, Academy of Sciences of the Ukrainian SSR, state that a rotating amalgamated silver electrode has properties very similar to those of a dropping mercury<sup>dropping</sup> electrode. In the experiments described in this paper, polarograms obtained with a dropping mercury<sup>dropping</sup> cathode are compared with polarograms obtained with either a stationary platinum needle cathode or a rotating platinum cathode of the same shape. As an anode mercury was used first, but later a silver plate was substituted for it. The low overvoltage of the platinum electrode proved to be a disadvantage. In order to increase the overvoltage, amalgamation of the surface was resorted to. Silver was used because it can be more easily and effectively amalgamated than platinum. This is the second communication on the subject by Skobets and his collaborators.

In the same issue of Zavodskaya Laboratoriya (pp. 138-143 and 144-148), two communications on the periodically dipping solid electrode and its application in polarography are published by Yu. S. Lyalikov and

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V. I. Karamsin of the Krivorog Mining and Ores Institute. In the first paper the authors describe a platinum needle electrode, which dips into the electrolyte, and is surrounded by a stream of gas (hydrogen) being bubbled through the solution in such a manner that each succeeding bubble <sup>pushes</sup> the solution away from the surface of the electrode (i.e., the surface of the electrode is alternately exposed to the gas and to the solution). The original model used by the authors had a mercury anode with a rather large surface. Using a cell of this type, the authors obtained polarograms which closely resemble those produced by a dropping mercury <sup>dropping</sup> cathode. Slow bubbling leads to considerable oscillations, so that determination of the height of the wave on the current strength - voltage diagram becomes difficult. Furthermore, the height of the wave is affected by the rate of bubbling, so that bubbling, besides being rapid, must be at a strictly constant rate. The wave height depends on the temperature, as in the customary type of polarographic cell. The temperature coefficient of this dependence, as determined in a 0.004 N cadmium chloride solution, is rather high and comprises

$$\frac{\Delta H}{\Delta t} = 4.45 \text{ mm. per degree} = 0.032 \text{ } \mu\text{ ampere per degree}$$

As expected, the height of the wave is affected by the type of anode which is used. Three types (a needle anode 14 millimeters long and having a diameter of 0.1 millimeters, a standard calomel half-cell, and a plain mercury electrode) have been tried. The needle anode was found to give a polarogram which is as distinct as that obtained with the plain mercury anode. The construction embodying the needle anode is shown in Figure 1 (reproduce Fig. 3, page 139). The diameter of the cathode gas outlet

caption: "Elect. L. Rev. with needle anode"

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tube and the volume of gas bubbles have no effect on the polarogram ( $\text{Cd Cl}_2$  and  $\text{Pb (NO}_3)_2$  solutions), but the depth of submersion of the cathode has ( $\text{CdCl}_2$  in  $\text{KCl}$  solution) and must be controlled. The effect of the depth of submersion of the needle anode on the wave height is still greater. As before, amalgamation of the surface of electrodes was found to be of advantage in the sense that overvoltage is greater and that clearer polarograms with a flatter plateau result.

As in the old type of polarographic cell, oxygen interferes with determinations and must be removed.

In the course of the work described in the first of their two papers, Lyalikov and Karasins took polarographs of lead, copper, and cadmium for the purpose of calibrating the new cell devised by them. They report that a linear dependence between the height of the polarographic wave and the concentration could be observed on all calibration curves. The editor of "Zavodskaya Laboratoriya" supplements this paper with a note to the effect that the use of solid electrodes will prove to be of particular advantage in analysing elements which cannot be determined by means of a dropping mercury cathode.

In the second paper of the series, Lyalikov and Karasins describe a determination of metal ion concentrations in salt melts, i.e. under conditions where the use of a <sup>drop</sup>dropping-mercury electrode would be impossible.

The special assembly of solid electrodes used in this case is shown in Figure 2 (reproduce Fig. 1, p. 144. Caption on the side of the drawing

should be "Gas"). Potassium nitrate was used as a suitable "background" solvent for  $\text{CuSO}_4$  and  $\text{CdCl}_2$ . During the determination the electrode assembly was dipped into a crucible containing molten potassium nitrate. Several other compounds ( $\text{KHSO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_7$ ,  $\text{KNO}_2$ ,  $\text{KOH}$ ,  $\text{NaNO}_2$ ,  $\text{NaOH}$ ) were also tested in regard to their suitability as solvents for polarographic work of this type.

Caption  
"Electrode  
Pair"

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$K_2S_2O_7$  was actually used as a solvent for  $CuSO_4$  and  $NiSO_4$ . It was found that neither nickel sulphate nor copper sulphate was dissociated into ions notwithstanding the good solubility of these salts in  $K_2S_2O_7$ . In  $KNO_3$  a determination of the phosphate ion could be carried out in addition to determinations of metal cations (in separate solutions). The plateau due to the phosphate ion in the polarogram taken on a  $Na_3PO_4-KNO_3$  melt could be suppressed by adding  $Ba(NO_3)_2$ . This suggests the possibility of carrying out titrations. The difficulties contingent on regulating the rate of bubbling, the depth of submersion of the electrodes, and the temperature could be successfully overcome by the authors in the series of preliminary experiments described here. Maxima arising in some polarograms could not be suppressed, however.

The authors do not state what gas they used in polarographic work on salt melts.

(Reproduce two drawings from original text)

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